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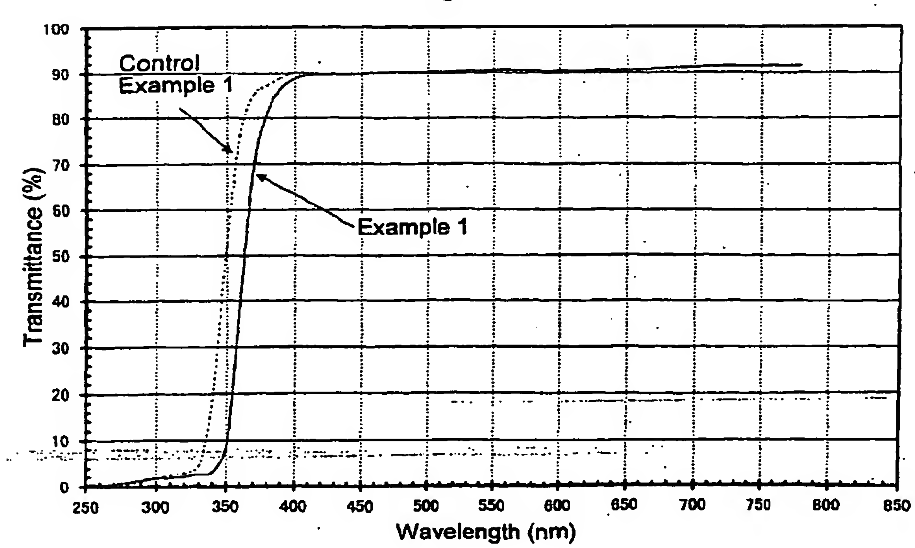
(54) ULTRAVIOLET-ABSORBING, COLORLESS, TRANSPARENT SODA-LIME SILICA GLASS

(57) An ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass as well as glass bottles formed out of the glass are disclosed which, while maintaining high transmittance to light in the visible region and thereby allowing the contents to be seen clearly, absorbs ultraviolet radiation and thus prevents coloration, discoloration, fading in color or deterioration of the flavor of the contents caused by ultraviolet radiation. The glass is characterized in that its composition includes, in % by weight, SO_3 ··· 0.15-0.4 %; Cerium oxide ··· 0.2-1 % (calculated as CeO_2); Fe_2O_3 ··· 0.01-0.08 %; FeO ··· 0-0.008 %; Manganese oxide ··· 0.01-0.08 % (calculated as MnO); and Cobalt oxide ··· 0-0.0005 % (calculated as CoO).

Fig. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to an ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass, as well as to glass bottles formed out of the glass. In more detail, the present invention relates to an ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass as well as to glass bottles formed out of the glass which has no greenish or bluish tint and which can prevent coloration, discoloration, fading in color or deterioration of the flavor of the contents caused by ultraviolet radiation and, inter alia, coloration of refined "sake", coloration or fading in color of wines, and deterioration of the flavor of refined "sake" and wines.

BACKGROUND ART

[0002] In order to prevent light-induced coloration, discoloration, fading in color or deterioration of the flavor of their content beverages, amber, green or blue bottles have been widely used for refined "sake" or for beer. All of those glass bottles are deeply colored, which prevent their contents from being seen clearly as they are through the bottles. Thus, there have been needs for transparent, colorless glass bottles with high brightness which thereby allow their contents to be seen more clearly.

[0003] In majority of cases, however, transparent, colorless glass with high brightness has, at the same time, high transmittance to ultraviolet radiation. Ultraviolet radiation passing through a glass bottle is apt to induce coloration, discoloration or fading in color of its contents. In the case where its content is refined "sake", inter alia, its flavor would be deteriorated along with a yellowing in color, thereby greatly impairing its commodity value. In the case of wines, there also are problems of their coloration or fading in color and deterioration of their flavor.

[0004] As a means to solve these problems, an ultraviolet radiation-absorbing, colorless soda-lime glass is disclosed in Japanese Unexamined Patent Publication No. S52-47812. In this patent, the glass contains CeO_2 and V_2O_5 as ultraviolet radiation absorbents, and MnO_2 or Se and, as needed, Co_3O_4 as decolorizing agents. This glass, however, runs a substantial risk of undergoing coloration as a result of solarization because of coexistence of CeO_2 and V_2O_5. Japanese Patent No. 2528579 and Japanese Laid-open Patent Publication No. H8-506314 disclose glasses absorbing ultraviolet and infrared radiation which contains Fe_2O_3, FeO, CeO_2 and manganese oxide. However, as these glasses have a high total iron content together with a high content of FeO, a green to blue color in these glasses is unavoidable. This renders those glasses unsatisfactory as glasses used for producing colorless, transparent bottles with high brightness that allow their contents to be seen more clearly.

[0005] Therefore, colorless, transparent, ultraviolet radiation-absorbing glass bottles have been needed which, while allowing their contents to be seen clearly on a store shelf due to their high transmittance to light in the visible region, enable to keep their contents from being exposed to ultraviolet radiation in the process of distribution and on a store shelf.

[0006] The objective of the present invention is to provide an ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass as well as to glass bottles formed out of the glass which, while maintaining high transmittance to light in the visible region and thereby allowing the contents to be seen clearly, absorbs ultraviolet radiation and thereby prevents coloration, discoloration, fading in color or deterioration of the flavor of the contents caused by ultraviolet radiation.

DISCLOSURE OF INVENTION

[0007] The present inventors found, as a result of repeated studies to reach the above objective, that an ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass is obtained which is highly absorptive of ultraviolet radiation while having high transmittance to visible light, by adding to a conventional basic composition of soda-lime-silica glass specific proportions of SO_3, cerium oxide, Fe_2O_3, FeO, manganese oxide and, as needed, cobalt oxide. The present invention was accomplished based on this finding.

[0008] Thus, the present invention provides an ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass which is characterized in that its composition includes, in % by weight,.

SO_3	0.15-0.4%
Cerium oxide	0.2 - 1 % (calculated as CeO_2)
Fe_2O_3	0.01 - 0.08 %
FeO	0 - 0.008 %
Manganese oxide	0.01 - 0.08 % (calculated as MnO), and

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(continued)

Cobalt oxide	0 - 0.0005 % (calculated as CoO).

[0009] Herein, "cerium oxide" means both of CeO_2 and Ce_2O_3, and its "% by weight" is expressed as a value obtainable when all the contained cerium oxide is replaced with CeO_2. Likewise, "manganese oxide" means both of MnO and Mn_2O_3, and its "% by weight" is expressed as a value obtainable when all the contained manganese oxide is replaced with MnO. In addition, "cobalt oxide" is also expressed as a value obtainable when all the contained cobalt oxide is replaced with CoO.

[0010] The present invention further provides a glass bottle formed out of the above-identified ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass.

[0011] As mentioned above, the compositional characteristic of the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of the present invention consists in that it contains, in specific proportions, SO_3, cerium oxide, Fe_2O_3, FeO, manganese oxide and, as needed, cobalt oxide. The basic composition of soda-lime-silica glass may be in a conventional range. However, considering needs for high chemical durability, eliminated possibility of devitrification and proper easiness of melting, it is preferable that the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of the present invention typically comprises, in % by weight:

SiO_2	65 - 75 %
Al_2O_3	0 - 5 %
CaO	6 - 15 %
MgO	0 - 4 %
Na_2O	10 - 17 %
K_2O	0 - 4 %
SO_3	0.15 - 0.4 %
Cerium oxide	0.2 - 1 % (calculated as CeO_2)
Fe_2O_3	0.01 - 0.08 %
FeO	0 - 0.008 %
Manganese oxide	0.01 - 0.08 % (calculated as MnO)
Cobalt oxide	0 - 0.0005 % (calculated as CoO).

[0012] In addition, to enhance the reliability of the total performance of the glass of the present invention, it is more preferable that the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of the present invention is characterized in that its composition includes, in % by weight,

SO_3	0.2 - 0.38 %
Cerium oxide	0.2 - 1 % (calculated as CeO_2)
Fe_2O_3	0.015 - 0.06 %
FeO	0 - 0.006 %
Manganese oxide	0.013 - 0.07 % (calculated as MnO), and
Cobalt oxide	0 - 0.0005 % (calculated as CoO).

[0013] Furthermore, to further enhance the reliability of the total performance of the glass of the present invention, it is most preferable that the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of the present invention is characterized in that its composition includes, in % by weight,

SO_3	0.24 - 0.35 %
Cerium oxide	0.3 - 0.8 % (calculated as CeO_2)
Fe_2O_3	0.02 - 0.04 %
FeO	0 - 0.004 %
Manganese oxide	0.02 - 0.05 % (calculated as MnO), and
Cobalt oxide	0 - 0.0003 % (calculated as CoO).

[0014] Furthermore, it is more preferable that the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of the present invention comprises, in % by weight:

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SiO_2	65 - 75 %
Al_2O_3	0 - 5 %
CaO	6 - 15 %
MgO	0 - 4 %
Na_2O	10 - 17 %
K_2O	0 - 4 %
SO_3	0.2 - 0.38 %
Cerium oxide	0.2 - 1 % (calculated as CeO_2)
Fe_2O_3	0.015 - 0.06 %
FeO	0 - 0.006 %
Manganese oxide	0.013 - 0.07 % (calculated as MnO)
Cobalt oxide	0 - 0.0005 % (calculated as CoO).

[0015] Still further, it is most preferable that the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of the present invention comprises, in % by weight:

SiO_2	68 - 74 %
Al_2O_3	1 - 4 %
CaO	8 - 13 %
MgO	0.1-3%
Na_2O	11 - 15 %
K_2O	0.1-3%
SO_3	0.24 - 0.35 %
Cerium oxide	0.3 - 0.8 % (calculated as CeO_2)
Fe_2O_3	0.02 - 0.04 %
FeO	0 - 0.004 %
Manganese oxide	0.02 - 0.05 % (calculated as MnO)
Cobalt oxide	0 - 0.0003 % (calculated as CoO).

[0016] On a transmittance curve obtained with a 3.5-mm thick sample, the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of the present invention preferably has transmittance of not more than 4.5 % at the wavelength of 330 nm and, in the visible region of 420-780 nm, transmittance of not less than 88 % without having absorption at any particular wavelength.

[0017] In addition, the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of the present invention preferably has dominant wavelength (λ_d) at 565-575 nm.

[0018] The ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of the present invention has an excellent ability to absorb ultraviolet radiation, in particular ultraviolet radiation at the wavelength of 330 nm. Therefore, when used in the form of glass bottles, it can prevent coloration, discoloration, fading in color or deterioration of the flavor of their contents caused by light, and is highly effective, inter alia, in preventing not only a yellowing in color and deterioration of the flavor of refined "sake", which is sensitive to ultraviolet radiation at wavelengths around 330 nm, but also coloration, fading in color or deterioration of the flavor of wines.

BRIEF DESCRIPTION OF DRAWINGS

[0019] Figure 1 is a graph illustrating the transmittance curves of the glasses of Example 1 and Control Example 1 in a wavelength range of 250-780 nm.

[0020] Figure 2 is a graph illustrating the transmittance curves of the glasses of Example 1 and Control Example 1 in a wavelength range of 250-400 nm.

BEST MODE FOR CARRYING OUT THE INVENTION

[0021] In general, SiO_2, which is a glass network-former, is contained preferably at a proportion of 65-75 % by weight. This is because a SiO_2 content below 65 % by weight might reduce chemical durability of the glass and, conversely, a SiO_2 content over 75 % by weight might render the glass prone to devitrification. Considering chemical durability and

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proneness to devitrification of the glass, it is more preferable that the content of SiO_2 is at a proportion of 68-74 % by weight.

[0022] Al_2O_3, which is an intermediate oxide of glass, serves to enhance chemical durability of the glass. Inclusion of Al_2O_3 is not essential. When it is included, it is generally preferable that its proportion is not more than 5 % by weight. This is because an Al_2O_3 content over 5 % by weight might render the glass difficult to melt. Considering chemical durability and ease of melting of the glass, it is more preferable that the content of Al_2O_3 is at a proportion of 1-4 % by weight.

[0023] CaO, which is a glass network-modifier, serves to enhance chemical durability of the glass as well as to improve its easiness of melting. In general, CaO is contained preferably at a proportion of 6-15 % by weight. This is because a CaO content below 6 % by weight might render the chemical durability insufficient, and, conversely, a CaO content over 15 % by weight might render the glass prone to devitrification. Considering chemical durability, proper ease of melting and proneness to devitrification of the glass, it is more preferable that the content of CaO is at a proportion of 8-13 % by weight.

[0024] MgO, which is a glass network-modifier, like CaO, serves to enhance chemical durability of the glass as well as to improve ease of melting. Inclusion of MgO is not essential. When it is included, it is generally preferable that its proportion is not more than 4 % by weight. This is because a MgO content over 4 % by weight might render the glass prone to devitrification. Considering chemical durability, ease of melting and proneness to devitrification of the glass, it is more preferable that the content of MgO is at a proportion of 0.1-3 % by weight.

[0025] Na_2O, which is a glass network-modifier, has an effect to promote melting of raw materials. Generally, Na_2O is contained preferably at a proportion of 10-17 % by weight. This is because a Na_2O content below 10 % by weight renders the glass difficult to melt, and, conversely, a Na_2O content over 17 % by weight might reduce chemical durability of the glass. Considering ease of melting and chemical durability of the glass, it is more preferable that the content of Na_2O is at a proportion of 11-15 % by weight.

[0026] K_2O, which is a glass network-modifier, serves like Na_2O to promote melting of raw materials. Inclusion of K_2O is not essential. When it is included, it is generally preferable that its proportion is not more than 4 % by weight. This is because a K_2O content over 4 % by weight renders the glass prone to devitrification. Considering ease of melting and proneness to devitrification of the glass, it is more preferable that the content of K_2O is at a proportion of 0.1-3 % by weight.

[0027] SO_3 may be a residue in the glass of the fining agents that were added to the batch as a combination of salt cake (sodium sulfate) and carbon. The amounts of salt cake, carbon and other oxidizing and reducing agents that govern the redox of the batch may be determined so that the content of SO_3 will fall within the range of 0.15-0.4 % by weight. The lower limit is set at 0.15 % by weight because a lower content of SO_3 in the glass would render the glass too reductive, which then would increase the ratio of FeO to Fe_2O_3 and decrease the ratio of Mn_2O_3 to MnO, even if desired amounts of cerium oxide and manganese oxide were added, thus giving the glass a greenish to bluish tint. The upper limit is set at 0.4 % by weight because higher content of SO_3 in the glass might cause seed to be left in the glass. Considering prevention of pale greenish to pale bluish coloration of the glass and removal of seed, it is preferable that the content of SO_3 in the glass is controlled to fall within the range of 0.2-0.38 % by weight, and it is more preferable within the range of 0.24-0.35 % by weight.

[0028] Cerium oxide serves as an absorbent for ultraviolet-radiation and is contained as CeO_2 and Ce_2O_3 in the glass of the present invention. Although the mutual proportion between CeO_2 and Ce_2O_3 varies depending on the content of SO_3 and therefore is not clear, they are contained preferably at 0.2-1 % by weight in total (but calculated as CeO_2). This is because a total content of cerium oxide below 0.2 % by weight might provide insufficient effect to absorb ultraviolet radiation, and, depending on the content of SO_3, might allow the ratio of FeO to Fe_2O_3 to increase, thereby giving the glass a bluish tint. It is also because, conversely, the glass would acquire an undesired fluorescent color when its content is over 1 % by weight. Considering the creation of an ultraviolet radiation-absorbing effect and prevention of emergence of fluorescence in the glass, it is more preferable that the total content of cerium oxide is at a proportion of 0.3-0.8 % by weight.

[0029] Fe_2O_3, like cerium oxide, has an ultraviolet radiation-absorbing effect. However, Fe_2O_3 can effectively absorb ultraviolet radiation around 330 nm, which cerium oxide by itself is unable to absorb sufficiently. Ultraviolet radiation at this wavelength is most relevant to the change in quality of refined "sake". Fe_2O_3 is contained preferably at a proportion of 0.01-0.08 % by weight. This is because a Fe_2O_3 content below 0.01 % by weight might provide the above effect only insufficiently, and, conversely, a Fe_2O_3 content over 0.08 % by weight might make it difficult for Mn^{3+} ion to decolorize yellow-green coloration caused by Fe^{3+} ion. Considering desirable absorption of ultraviolet radiation by the glass, in particular around 330 nm, and prevention of coloration, it is more preferable that the content of Fe_2O_3 is at a proportion of 0.015-0.06 % by weight, and it is still more preferable at a proportion of 0.02-0.04 % by weight.

[0030] FeO is a component which is inevitably produced during the glass melting process from contaminant iron in silica sand in the glass batch, or from iron added as Fe_2O_3 to the batch. FeO is not only an unnecessary component for obtaining the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of the present invention,

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but its content must be not more than 0.008 % by weight. This is because a FeO content over 0.008 % by weight might give the glass a bluish tint. In order to constantly obtain colorless and transparent glass without fail, it is preferable that the content of FeO is not more than 0.006 % by weight, and it is more preferable not more than 0.004 % by weight.

[0031] Manganese oxide, which is an essential component for decolorizing the yellow-green coloration caused by Fe_2O_3 contained as an ultraviolet radiation absorbent, is contained preferably at 0.01-0.08 % by weight in accordance with the above-described contents of SO_3, cerium oxide, Fe_2O_3 and FeO. Although manganese oxide is present in the glass both as MnO and Mn_2O_3, at unknown mutual proportion, it is Mn^{3+} ion that has a decolorizing effect. The above-described content of manganese oxide is the sum of MnO and Mn_2O_3 (but calculated as MnO). A total content of manganese oxide below 0.01 % by weight might provide an insufficient decolorizing effect. Conversely, a total content of manganese oxide over 0.08 % by weight might lead to red-purple coloration due to excessive Mn^{3+} ion that cannot be fully decolorized even by inclusion of cobalt oxide as mentioned below or, even if it is successfully decolorized, might reduce the brightness of the glass, thereby impairing its transparent appearance. Considering decolorizing effect, it is more preferable that the total content of manganese oxide is at a proportion of 0.013-0.07 % by weight, and it is still more preferable at a proportion of 0.02-0.05 % by weight.

[0032] Cobalt oxide has an effect to decolorize red-purple coloration due to Mn^{3+} ion. Addition of cobalt oxide is not essential. Where somewhat excess Mn^{3+} ion is present, cobalt oxide may be added as needed at or below 0.0005 % by weight (calculated as CoO) to decolorize red-purple coloration due to Mn^{3+} ion. A total content of cobalt oxide over 0.0005 % by weight might reduce the brightness of the glass, thereby impairing its transparent appearance. Considering the transparent appearance of the glass, it is preferable that the total content of cobalt oxide is not more than 0.0003 % by weight.

[0033] According to the above range of composition, an ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass can be obtained which, on a transmittance curve obtained with a 3.5-mm thick sample, has transmittance of not more than 4.5 % at the wavelength of 330 nm and, in the visible region of 420-780 nm, transmittance of not less than 88 % without having absorption at any particular wavelength. Keeping the transmittance at or below 4.5 % at the wavelength of 330 nm is particularly effective in preventing a yellowing in color and deterioration of the flavor of refined "sake". More preferably, the transmittance at the wavelength of 330 nm is not more than 4 %.

[0034] It is preferable that the dominant wavelength (λ_d) of the glass of the present invention is 565-575 nm. This is because this type of glass, which has no absorption at any particular wavelength in the visible region, would have a bluish tint when its dominant wavelength (λ_d) is below 565 nm, and a reddish tint where it is over 575 nm. To be completely colorless and transparent, the dominant wavelength (λ_d) of the glass of the present invention is more preferably 567-573 nm.

[0035] A general method of producing the glass and glass bottles of the present invention is as follows. Briefly, to 100 parts by weight of silica sand are added 25-36 parts by weight of soda ash, 23-33 parts by weight of limestone, 0.03-0.15 part by weight of carbon (85 % by weight of purity), 0.7-2.0 parts by weight of salt cake (sodium sulfate), 0.26-1.4 parts by weight of cerium oxide (as CeO_2) and 0-0.08 part by weight of iron oxide (added as Fe_2O_3 when the amount of contaminant iron in the silica sand is insufficient), the last two of which, i.e., cerium oxide and iron oxide, serve as ultraviolet radiation absorbents, and 0.015-0.17 part by weight of manganese oxide (as MnO_2 of 80 % by weight of purity) and 0-0.0007 part by weight of cobalt oxide (as Co_3O_4), the last two of which, i.e., manganese oxide and cobalt oxide, serve as decolorizing agents, and thus prepared batch composition is melted at 1400-1500 °C, then adjusted to 1200-1350 °C in a working end, passed through a feeder and then into a molding machine, where the glass is formed into bottles at a temperature range of 700-1000 °C. Formed bottles are introduced into an annealing lehr so that strain is removed at 500-600 °C, and cooled over 30 min to 2 hrs to ambient temperature to provide the final product.

[0036] Although soda-lime-silica glass usually contains as a component several % by weight of Al_2O_3, other raw materials such as alumina, aluminium hydroxide and feldspar may be further added to adjust the composition when the amount of the contaminant alumina component in the silica sand is insufficient.

[0037] Where cullet is employed, blending proportions of the batch may be modified in accordance with the amounts of SO_3, cerium oxide, iron oxide, manganese oxide and cobalt oxide contained in the cullet.

EXAMPLES

[0038] The present invention is described in further detail below with reference to examples. However, it is not intended that the present invention be limited to the examples.

[0039] In the examples and the control examples, brightness (Y), dominant wavelength (λ_d), excitation purity (Pe) were calculated by the CIE method provided in JIS Z 8701 based on transmittance curves obtained by measuring 3.5-mm thick, polished samples on a spectrophotometer [U-3410, manufactured by HITACHI, LTD.] and converting the values into those corresponding to 10-mm thick samples.

[0040] Compositional analysis of the glass was made on a X-ray fluorescence analyzer (3070: manufactured by RIGAKU). The proportion between Fe_2O_3 and FeO was calculated based on the absorbance measured at the wave-

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length of 1000 nm on the spectrophotometer.

[Example 1]

[0041] A batch composition was prepared by weighing and mixing the following components.

Kemerton silica sand	100 parts by weight
Soda ash	27.5 parts by weight
Limestone	27.5 parts by weight
Salt cake (sodium sulfate)	1.6 parts by weight
Carbon (85 % by weight of purity)	0.06 part by weight
CeO_2	0.85 part by weight
MnO_2 (80 % by weight of purity)	0.06 part by weight
Co_3O_4	0.00015 part by weight

[0042] The obtained batch composition was introduced into a continuous tank furnace having a melting capacity of 150 t/day and melted at a glass melting temperature of 1450 °C for 38 hours, then passed through a feeder at 1270 °C, molded and passed along a line equipped with a conventional annealing lehr to obtain bottles having a capacity of 300 mL.

[0043] A sample for measurement was cut out of a glass bottle thus obtained, polished and measured to obtain a transmittance curve on the spectrophotometer. The transmittance curve thus obtained is shown in Figures 1 and 2. This glass bottle, as calculated for sample thickness of 10 mm, had brightness (Y) of 87.0 %, dominant wavelength (λ_d) of 572.5 nm, and excitation purity (Pe) of 1.1 %. In addition, its transmittance at 330 nm was 2.8 %. Furthermore, in the visible region of 420-780 nm, its transmittance was not less than 88 % without any apparent rise or fall in absorption at a particular wavelength. Thus, this glass bottle is proved to have an excellent ability to absorb ultraviolet radiation while being colorless and transparent.

[0044] Compositional analysis of this glass by X-ray fluorescence spectrometry (but by spectrophotometry with regard to the proportion between Fe_2O_3 and FeO) gave the following proportions (% by weight) in the composition.

SiO_2	71%
Al_2O_3	2%
CaO	11.3%
MgO	0.15 %
Na_2O	12.5%
K_2O	1.4%
SO_3	0.30%
Cerium oxide	0.65 % (calculated as CeO_2)
Fe_2O_3	0.028%
FeO	0.0018%
Manganese oxide	0.030 % (calculated as MnO)
Cobalt oxide	0.00012 % (calculated as CoO)

[Control Example 1]

[0045] A batch composition was prepared by weighing and mixing the following components. Using this batch composition, glass bottles were produced by the same method as in Example 1, which had a capacity of 300 mL.

Kemerton silica sand	100 parts by weight
Soda ash	27.5 parts by weight
Limestone	27.5 parts by weight
Salt cake (sodium sulfate)	1.6 parts by weight
Carbon (85 % by weight of purity)	0.06 part by weight
CeO_2	0.15 part by weight
MnO_2 (80 % by weight of purity)	0.045 part by weight

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(continued)

Co_3O_4	0.00015 part by weight

[0046] A transmittance curve was obtained with the glass bottles of the Control Example 1 above in the same manner as in Example 1. The transmittance curve thus obtained is shown in Figures 1 and 2. Color analysis carried out in the same manner showed that it had brightness (Y) of 86.6 %, dominant wavelength (λ_d) of 560.6 nm and excitation purity (Pe) of 0.41 %. Transmittance at 330 nm was 5.0 %. Furthermore, although the transmittance was not less than 88 % in the visible region of 420-780 nm, the transmittance at the range of 650-780 nm was lower by about 2 % than that obtained in Example 1. These data indicate that the glass bottle of Control Example 1 has insufficient ability to absorb ultraviolet radiation, in particular around 330 nm, and has a somewhat bluish tint.

[0047] Compositional analysis of the glass of Control Example 1 by X-ray fluorescence spectrometry (but by spectrophotometry with regard to the proportion between Fe_2O_3 and FeO) gave the following proportions (% by weight) in the composition.

SiO_2	71%
Al_2O_3	2%
CaO	11.3 %
MgO	0.15 %
Na_2O	12.5 %
K_2O	1.4 %
SO_3	0.25 %
Cerium oxide	0.11 % (calculated as CeO_2)
Fe_2O_3	0.021 %
FeO	0.006 %
Manganese oxide	0.027 % (calculated as MnO)
Cobalt oxide	0.00012 % (calculated as CoO)

[Control Example 2]

[0048] A batch composition was prepared by weighing and mixing the following components. Using this batch composition, glass bottles were produced by the same method as in Example 1, which had a capacity of 300 mL.

Kemerton silica sand	100 parts by weight
Soda ash	27.5 parts by weight
Limestone	27.5 parts by weight
Salt cake (sodium sulfate)	1.0 parts by weight
Carbon (85 % by weight of purity)	0.06 part by weight
CeO_2	0.26 part by weight
MnO_2 (80 % by weight of purity)	0.05 part by weight
Co_3O_4	0.0001 part by weight

[0049] A transmittance curve was obtained with the glass bottles of the Control Example 2 above in the same manner as in Example 1, and color analysis carried out in the same manner, showing that it had brightness (Y) of 88.9 %, dominant wavelength (λ_d) of 561.8 nm and excitation purity (Pe) of 0.71 %. Transmittance at 330 nm was 3.6 %. Furthermore, within the visible region of 420-780 nm, transmittance around 420-500 nm slightly increased. This indicates that the glass bottles of Control Example 2 has a slightly bluish tint.

[0050] Compositional analysis of the glass of Control Example 2 by X-ray fluorescence spectrometry (but by spectrophotometry with regard to the proportion between Fe_2O_3 and FeO) gave the following proportions (% by weight) in the composition.

SiO_2	71 %
Al_2O_3	2 %
CaO	11.3 %

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(continued)

MgO	0.15 %
Na_2O	12.5 %
K_2O	1.4%
SO_3	0.19 %
Cerium oxide	0.20 % (calculated as CeO_2)
Fe_2O_3	0.022 %
FeO	0.009 %
Manganese oxide	· 0.025 % (calculated as MnO)
Cobalt oxide	· 0.0001 % (calculated as CoO)

[Examples 2-15]

[0051] Glass bottles were produced in the same manner as in Example 1 except for modifications of blending proportions of batches.

[0052] The batch composition, glass composition, color and transmittance of each of Examples 1-15 and Control Examples 1 and 2 are shown collectively in Tables 1-3 below. In those tables, the color values are those calculated for sample thickness of 10 mm, and the values of transmittance are those obtained by measurement with 3.5-mm thick samples. From these tables, the glass of any of Examples 1-15 was confirmed to have an excellent ability to absorb ultraviolet radiation while being colorless and transparent.

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Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5
Batch composition (part(s) by weight)	Kemerton silica sand	100	100	100	100	100
	Soda ash	27.5	27.5	27.5	27.5	27.5
	Limestone	27.5	27.5	27.5	27.5	27.5
	Salt cake	1.6	1.4	1.4	1.4	1.4
	Carbon (85 %)	0.06	0.03	0.06	0.06	0.06
	CeO_2	0.85	0.80	0.80	0.80	0.80
	MnO_2 (80 %)	0.06	0.05	0.03	0.05	0.07
	Co_3O_4	0.00015	–	–	–	–
Glass composition (% by weight)	SiO_2	71	71	71	71	71
	Al_2O_3	2	2	2	2	2
	CaO	11.3	11.3	11.3	11.3	11.3
	MgO	0.15	0.15	0.15	0.15	0.15
	Na_2O	12.5	12.5	12.5	12.5	12.5
	K_2O	1.4	1.4	1.4	1.4	1.4
	SO_3	0.30	0.34	0.23	0.27	0.29
	Cerium oxide (calculated as CeO_2)	0.65	0.59	0.60	0.60	0.60
	Fe_2O_3	0.028	0.028	0.028	0.028	0.028
	FeO	0.0018	0.0017	0.0018	0.0017	0.0016
	Manganese oxide (calculated as MnO)	0.030	0.024	0.012	0.024	0.037
	Cobalt oxide (calculated as CoO)	0.00012	–	–	–	–
Color values	Y (%)	87.0	87.7	88.6	88.0	87.6
	λ_d (nm)	572.5	573.3	569.3	571.6	572.9
	Pe (%)	1.1	1.5	1.3	1.3	1.4
Transmittance (%) (330 nm)		2.8	3.1	3.2	3.3	3.2
Transmittance (%) (420~780 nm)		>88	>88	>88	>88	>88

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Table 2

		Example 6	Example 7	Example 8	Example 9	Example 10
Batch composition (part(s) by weight)	Kemerton silica sand	100	100	100	100	100
	Soda ash	27.5	27.5	27.5	27.5	27.5
	Limestone	27.5	27.5	27.5	27.5	27.5
	Salt cake	1.4	1.4	1.4	1.5	1.6
	Carbon (85 %)	0.06	0.05	0.04	0.06	0.06
	CeO_2	0.26	0.26	0.26	0.26	0.26
	MnO_2 (80 %)	0.03	0.05	0.05	0.05	0.05
	Co_3O_4	–	–	–	–	–
Glass composition (% by weight)	SiO_2	71	71	71	71	71
	Al_2O_3	2	2	2	2	2
	CaO	11.3	11.3	11.3	11.3	11.3
	MgO	0.15	0.15	0.15	0.15	0.15
	Na_2O	12.5	12.5	12.5	12.5	12.5
	K_2O	1.4	1.4	1.4	1.4	1.4
	SO_3	0.21	0.24	0.29	0.23	0.28
	Cerium oxide (calculated as CeO_2)	0.20	0.20	0.20	0.20	0.20
	Fe_2O_3	0.026	0.027	0.027	0.027	0.029
	FeO	0.0036	0.0035	0.0027	0.0027	0.0015
	Manganese oxide (calculated as MnO)	0.013	0.024	0.026	0.025	0.025
	Cobalt oxide (calculated as CoO)	–	–	–	–	–
Color values	Y (%)	89.2	89.1	88.9	89.1	88.7
	λ_d (nm)	567.0	565.5	567.8	565.6	569.7
	Pe (%)	0.83	0.79	0.85	0.79	1.0
Transmittance (%) (330 nm)		3.4	3.7	3.7	3.9	3.9
Transmittance (%) (420～780 nm)		>88	>88	>88	>88	>88

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Table 3

		Example 11	Example 12	Example 13	Example 14	Example 15	Control example 1	Control example 2
Batch composition (part(s) by weight)	Kemerton silica sand	–	100	100	100	100	100	100
	Sarawaku silica sand	100	–	–	–	–	–	–
	Soda ash	27.5	27.5	27.5	27.5	27.5	27.5	27.5
	Limestone	27.5	27.5	27.5	27.5	27.5	27.5	27.5
	Salt cake	1.4	1.4	1.2	0.7	1.4	1.6	1.0
	Carbon (85 %)	0.04	0.04	0.03	0.15	0.04	0.06	0.06
	CeO_2	0.53	0.81	1.08	1.08	0.81	0.15	0.26
	Fe_2O_3	–	0.042	0.014	–	0.065	–	–
	MnO_2 (80 %)	0.12	0.07	0.05	0.05	0.13	0.045	0.05
	Co_3O_4	0.00026	–	–	0.0001	0.0001	0.00015	0.0001
Glass composition (% by weight)	SiO_2	72	71	71	71	71	71	71
	Al_2O_3	2	2	2	2	2	2	2
	CaO	11.5	11.3	11.3	11.3	11.3	11.3	11.3
	MgO	0.15	0.15	0.15	0.15	0.15	0.15	0.15
	Na_2O	12.7	12.5	12.5	12.5	12.5	12.5	12.5
	K_2O	0.1	1.4	1.4	1.4	1.4	1.4	1.4
	SO_3	0.29	0.32	0.39	0.17	0.30	0.25	0.19
	Cerium oxide (calculated as CeO_2)	0.40	0.61	0.81	0.80	0.62	0.11	0.20
	Fe_2O_3	0.019	0.058	0.039	0.027	0.075	0.021	0.022
	FeO	0.0008	0.0016	0.0006	0.003	0.002	0.006	0.009
	Manganese oxide (calculated as MnO)	0.067	0.037	0.024	0.025	0.072	0.027	0.025
	Cobalt oxide (calculated as CoO)	0.0002	–	–	0.0001	0.0001	0.00012	0.0001
Color values	Y (%)	85.5	86.8	86.6	86.0	86.1	86.6	88.9
	λ_d (nm)	575.0	570.8	572.3	571.0	573.5	560.6	561.8
	Pe (%)	1.2	1.3	1.8	1.9	1.5	0.41	0.71
Transmittance (%) (330 nm)		3.2	2.6	2.5	2.9	2.4	5.0	3.6
Transmittance (%) (420～780 nm)		>88	>88	>88	>88	>88	>88	>88

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INDUSTRIAL APPLICABILITY

[0053] The present invention enables production of ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass and glass bottles formed out of the glass which, while having high transmittance to light in the visible region, absorbs ultraviolet radiation. Therefore, it is applicable to production of glass bottles which can prevent coloration, discoloration, fading in color or deterioration of the flavor of the contents, inter alia, glass bottles which can prevent a yellowing in color of refined "sake" and coloration or fading in color of wines, as well as deterioration of the flavor of refined "sake" and wines.

Claims

1. An ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass which is characterized in that its composition includes, in % by weight,

SO_3	0.15-0.4%
Cerium oxide	0.2 - 1 % (calculated as CeO_2)
Fe_2O_3	0.01 - 0.08 %
FeO	0 - 0.008 %
Manganese oxide	0.01 - 0.08 % (calculated as MnO), and
Cobalt oxide	0 - 0.0005 % (calculated as CoO).

2. An ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass which is characterized in that its composition includes, in % by weight,

SO_3	0.2 - 0.38 %
Cerium oxide	0.2 - 1 % (calculated as CeO_2)
Fe_2O_3	0.015 - 0.06 %
FeO	0 - 0.006 %
Manganese oxide	0.013 - 0.07 % (calculated as MnO), and
Cobalt oxide	0 - 0.0005 % (calculated as CoO).

3. An ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass comprising, in % by weight:

SiO_2	65 - 75 %
Al_2O_3	0 - 5 %
CaO	6 - 15 %
MgO	0 - 4 %
Na_2O	10 - 17 %
K_2O	0 - 4 %
SO_3	0.15 - 0.4 %
Cerium oxide	0.2 - 1 % (calculated as CeO_2)
Fe_2O_3	0.01 - 0.08 %
FeO	0 - 0.008 %
Manganese oxide	0.01 - 0.08 % (calculated as MnO)
Cobalt oxide	0 - 0.0005 % (calculated as CoO).

4. An ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass comprising, in % by weight:

SiO_2	65 - 75 %
Al_2O_3	0 - 5 %
CaO	6- 15%
MgO	0 - 4%
Na_2O	10 - 17 %

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(continued)

K_2O	0 - 4 %
SO_3	0.2 - 0.38 %
Cerium oxide	0.2 - 1 % (calculated as CeO_2)
Fe_2O_3	0.015 - 0.06 %
FeO	0 - 0.006 %
Manganese oxide	0.013 - 0.07 % (calculated as MnO)
Cobalt oxide	0 - 0.0005 % (calculated as CoO).

5. An ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass comprising, in % by weight:

SiO_2	68 - 74 %
Al_2O_3	1 - 4 %
CaO	8 - 13 %
MgO	0.1 - 3 %
Na_2O	11 - 15%
K_2O	0.1-3%
SO_3	0.24 - 0.35 %
Cerium oxide	0.3 - 0.8 % (calculated as CeO_2)
Fe_2O_3	0.02 - 0.04 %
FeO	0 - 0.004 %
Manganese oxide	0.02 - 0.05 % (calculated as MnO)
Cobalt oxide	0 - 0.0003 % (calculated as CoO).

6. The ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of one of claims 1 to 5 which has, on a transmittance curve obtained with a 3.5-mm thick sample, transmittance of not more than 4.5 % at the wavelength of 330 nm and has, in the visible region of 420-780 nm, transmittance of not less than 88 % without having absorption at any particular wavelength.

7. The ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of one of claims 1 to 5 which has dominant wavelength (λ_d) at 565-575 nm.

8. The ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of claim 6 which has dominant wavelength (λ_d) at 565-575 nm.

9. A glass bottle formed out of the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of one of claims 1 to 5.

10. A glass bottle formed out of the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of claim 6.

11. A glass bottle formed out of the ultraviolet radiation-absorbing, colorless, transparent soda-lime-silica glass of claim 7.

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Fig. 1

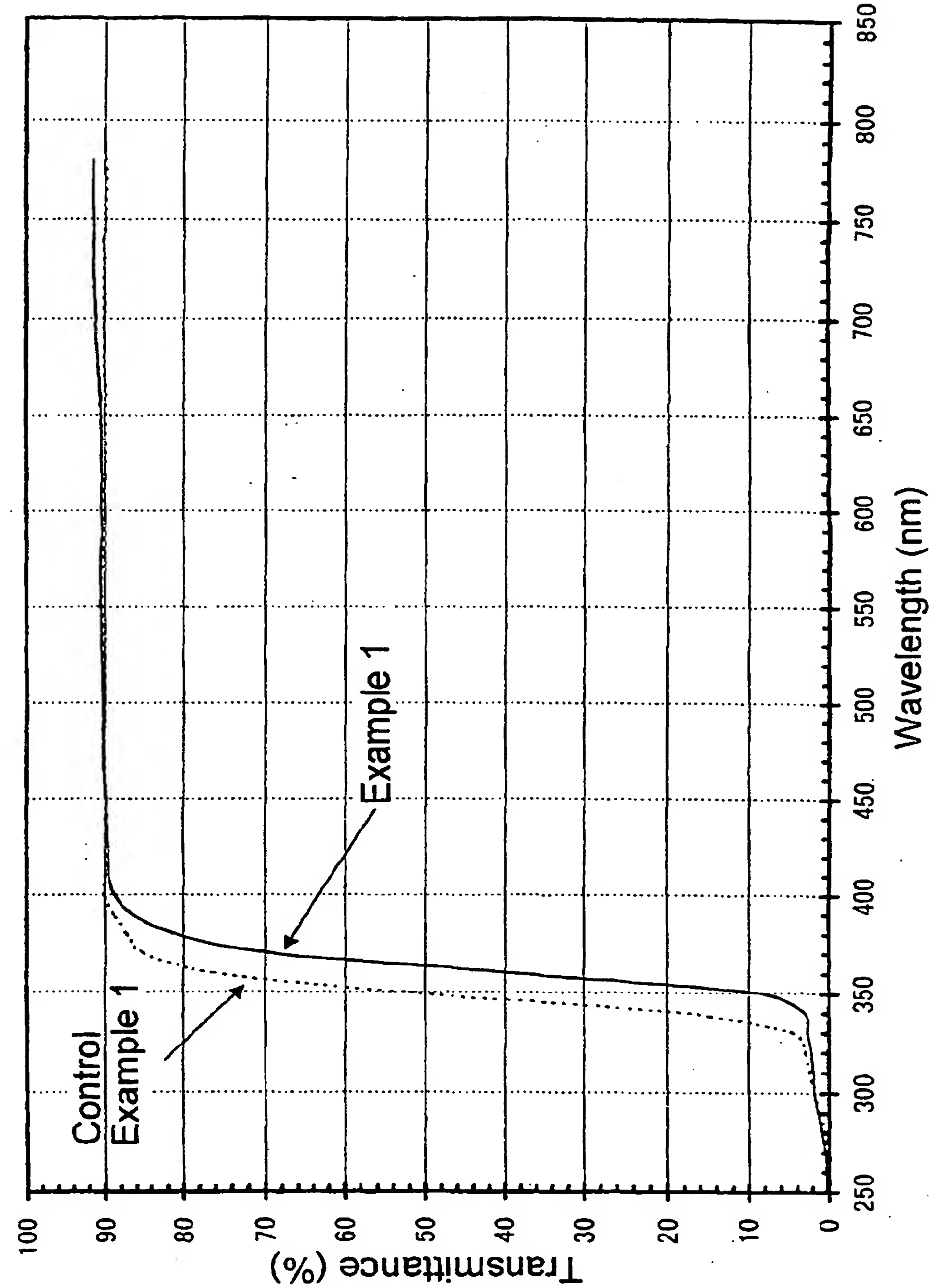

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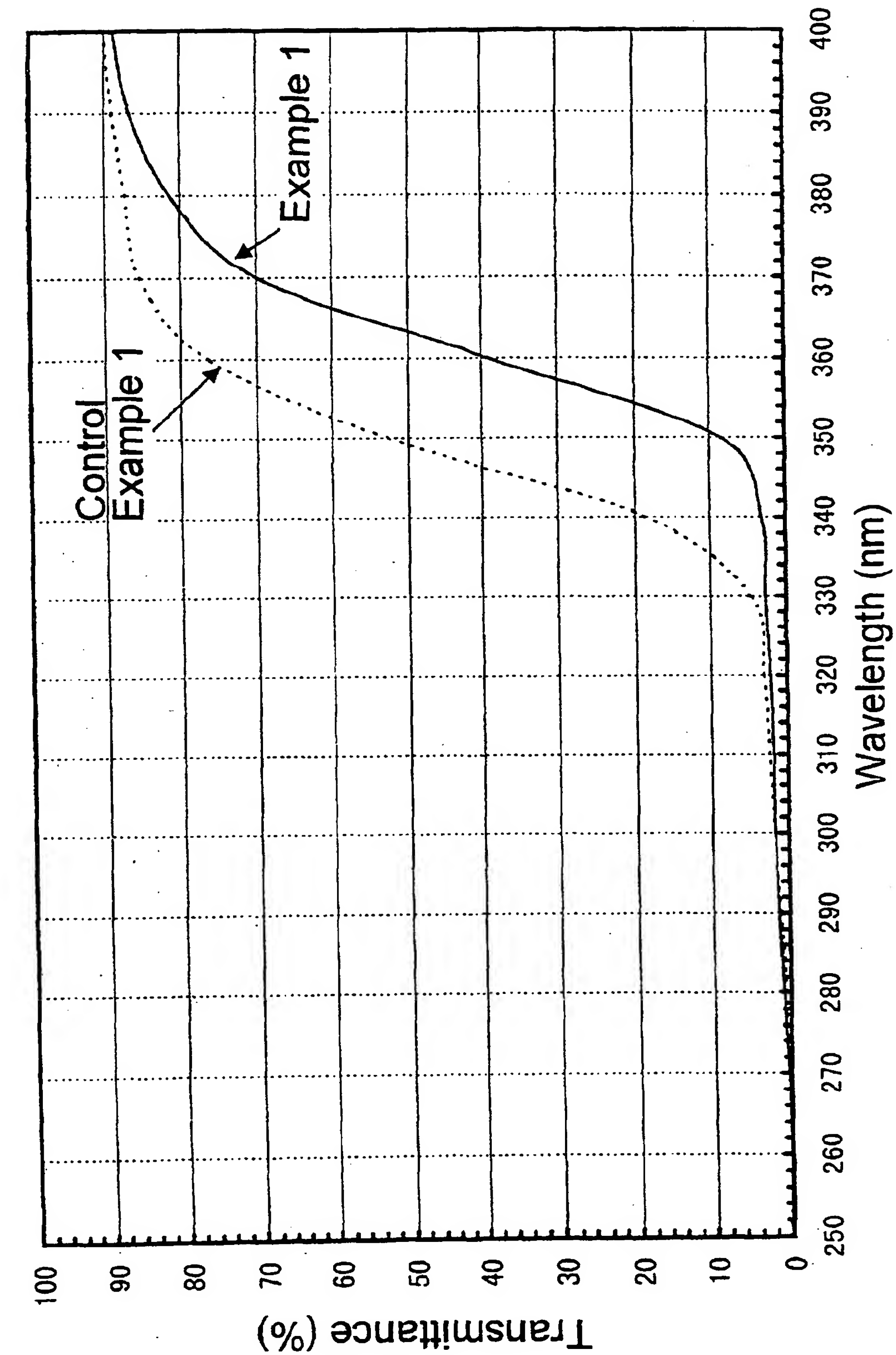
Fig. 2



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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/04564

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[6] C03C4/08 C03C3/095

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[6] C03C3/00-4/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-1999
Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI/L
(IC=C03C-003 OR IC=C03C-004) AND (FE? OR IRON?) AND (MN? OR MANGAN?) AND (CE? OR CERIUM?) AND (LIME? OR ULTRAVIOLET? OR ULTRA-VIOLET? OR UV?)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 10-226534, A (Central Glass Co., Ltd.), 25 August, 1998 (25.08.98), Claims 1 to 4; Par. Nos. [0020]-[0021], [0038] (Family: none)	1-11
A	JP, 10-218642, A (Central Glass Co., Ltd.), Par. No. [0018]-[0020], [0026] (Family: none)	1-11
A	JP, 5-178639, A (Central Glass Co., Ltd.), 20 July, 1993 (20.07.93), Claims 1, 2; Par. Nos. [0016] to [0018] & EP, 555552, A1	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 November, 1999 (11.11.99)	24 November, 1999 (24.11.99)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
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